UDC 666.32:666.3.022.12:666.3.015.4

SINTERING QUALITY OF CLAY MATERIALS

D. V. Abdrakhimov,[1] E. S. Abdrakhimova,[1] and V. Z. Abdrakhimov[1]

Translated from Steklo i Keramika, No. 6, pp. 25 – 27, June, 1999.

The effect of montmorillonite on sintering of kaolin and kaolinite-montmorillonite argillaceous materials from East Kazakhstan is studied. It is established that the optimum quantity of the introduced montmorillonite (30%) intensifies the sintering of clay materials.

The investigation of clays from numerous deposits established that the sintering quality of clays is determined by their chemical and mineralogic composition. In the production of floor tiles it is necessary to use clays with a high sintering capacity.

Clay deposits with good sintering qualities are non-existent or limited in the greater part of Kazakhstan, as well as the Central Asian republics and the eastern part of Russia. The conversion of floor tile production in East Kazakhstan to efficient up-to-date technology will require the use of local clays that do not sinter up to a temperature of 1300°C.

It is known that sintering of kaolinite-montmorillonite clays depends on the kaolinite : montmorillonite ratio. The best sinterability is observed in clays whose ratio of the specified components ranges from 4 to 7 [1]. In this context, the sintering of kaolinite clay/bentonite mixtures under accelerated firing conditions and the development of low-temperature mixtures on this basis hold special interest.

The materials selected for the investigation were kaolinite clays from the Zhana-Daurskii and Mitrofanovskii deposits, the argillaceous component of zircon-ilmenite gravitation tails, and Taganskii bentonite. The chemical and mineralogic compositions of the considered materials are given in Tables 1 and 2.

The mixtures were prepared by the slip method. The samples were fired in the accelerated regime for 1 h at a temperature of 1150°C. The results of the experiments are shown in Fig. 1. As can be seen, the water absorption of fired samples of different compositions is lower in the range where the montmorillonite content is higher. The compositions of the ceramic mixtures and the kaolinite : montmorillonite ratios are shown in Table 3.

Montmorillonite does not have a significant effect on the sintering of the clay component of the zircon-ilmenite ore gravitation tails. An introduction of up to 30% montmorillonite to the clay component insignificantly decreases the water absorption: from 3.0 to 2.6%. A further increase in the montmorillonite content under accelerated firing conditions at a temperature of 1150°C results in the swelling of samples, which leads to an increase in the water absorption (Fig. 1, curve *1*).

The Taganskii bentonite does not have a perceptible effect on the nonsintering Mitrofanovskii kaolinite [2]. A montmorillonite additive to the Mitrofanovskii kaolin does not

[1] Nauka Production Company, East-Kazakhstan Technical University, Kazakhstan.

TABLE 1

Component	Mass content, %							Refractoriness, °C	Plasticity
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	calcination loss		
Argillaceous component of zircon-ilmenite ore gravitation tails	58.74	21.39	6.21	1.70	1.22	1.62	7.34	1480 – 1560	20 – 25
Clay:									
Zhana-Daurskii	69.14	17.38	3.10	2.00	1.42	0.20	6.08	1540 – 1570	12 – 18
Mitrofanovskii	63.34	21.97	2.08	1.02	0.82	4.48	4.55	1360 – 1420	9 – 15
Taganskii bentonite	59.60	18.21	4.51	1.93	3.30	1.28	7.70	1220 – 1250	35 – 45

cause sintering of the samples at the temperature 1150°C (the sintering of the crock does bring the water absorption below 5%, Fig. 1, curve *2*), since it apparently contains a considerable amount of montmorillonite.

Introduction of montmorillonite to the Zhana-Daurskii clay has a perceptible positive effect: when up to 30% montmorillonite is added, the clay become sinterable at the temperature 1150°C and the water absorption decreases from 5% to 2.5% (Fig. 1, curve *3*).

The investigation indicated that the optimum kaolinite : montmorillonite ratio for the considered argillaceous materials from East Kazakhstan should be within the limits of 0.90 – 1.45. Within this range, montmorillonite brings about a decrease in water absorption. The optimum amount of Taganskii bentonite is 30%.

In order to obtain the most complete data on the sintering quality of the argillaceous materials, the microstructure of the samples (Fig. 2) was studied using an EVM-100 BR electron microscope ("transmission" method, platinum-carbon replica). The electron microscope photos of the gravitation tails clay component (Table 3, mixture 1) reveal the concentration of the mullite-type component (Fig. 2*a*). Such microstructures serve for mullite penetration.

Along with the needle-shaped crystals, short prismatic mullite crystals were identified as well in the fired samples. The unusual shape of the mullite crystals is related to the content of Fe_2O_3 and TiO_2 in the gravitation tails clay component [3, 4]. With the emergence of the solid substitution

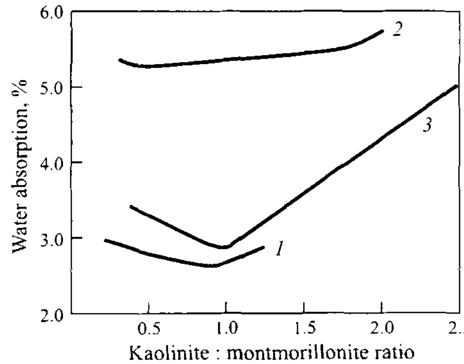

Fig. 1. Variation in water absorption of mixtures depending on the kaolinite : montmorillonite ratio: *1*) Argillaceous component of zircon-ilmenite ore gravitation tails — Taganskii bentonite; *2*) Mitrofanovskii clay — Taganskii bentonite; *3*) Zhana-Daurskii clay — Taganskii bentonite.

solution, mullite of various chemical compositions is formed. In this case, Fe^{3+} replaces Al^{3+}, and Ti^{4+} replaces Si^{4+}. The incorporation of iron and titanium oxides in the solid solution leads to the crystallization of mullite in the form of isometric grains and short prismatic crystals instead of extremely thin needles and elongated prismatic crystals [3, 4].

The introduction of the optimum (30%) amount of bentonite to the gravitation tails clay component (Table 3, mixture 5) intensified the formation of the liquid phase, which decreased water absorption. The electron microscope photos

TABLE 2

Component	Mass content, %									
	calcite	quartz	feldspar	montmorillonite	ilmenite	kaolinite	iron oxides	zircon	mica	pyroxene
Argillaceous component of zircon-ilmenite ore gravitation tails	2	17	18	10	2	40	3	2	–	–
Kaolin:										
Zhana-Daurskii	4	20	26	–	–	50	–	–	–	–
Mitrofanovskii	2	10	40	–	–	40	3	–	2	3
Taganskii bentonite	2	10	5	80	–	–	3	–	–	–

TABLE 3

Component	Mass content (%) in mixtures											
	1	2	3	4	5	6	7	8	9	10	11	12
Argillaceous component of zircon-ilmenite ore gravitation tails	100	–	–	80	70	60	–	–	–	–	–	–
Clay:												
Mitrofanovskii	–	100	–	–	–	–	80	70	60	–	–	–
Zhana-Daurskii	–	–	100	–	–	–	–	–	–	80	70	60
Taganskii bentonite	–	–	–	20	30	40	20	30	40	20	30	40
Kaolinite : montmorillonite ratio	–	–	–	1.33	0.90	0.44	2.00	1.16	0.50	2.50	1.45	0.62

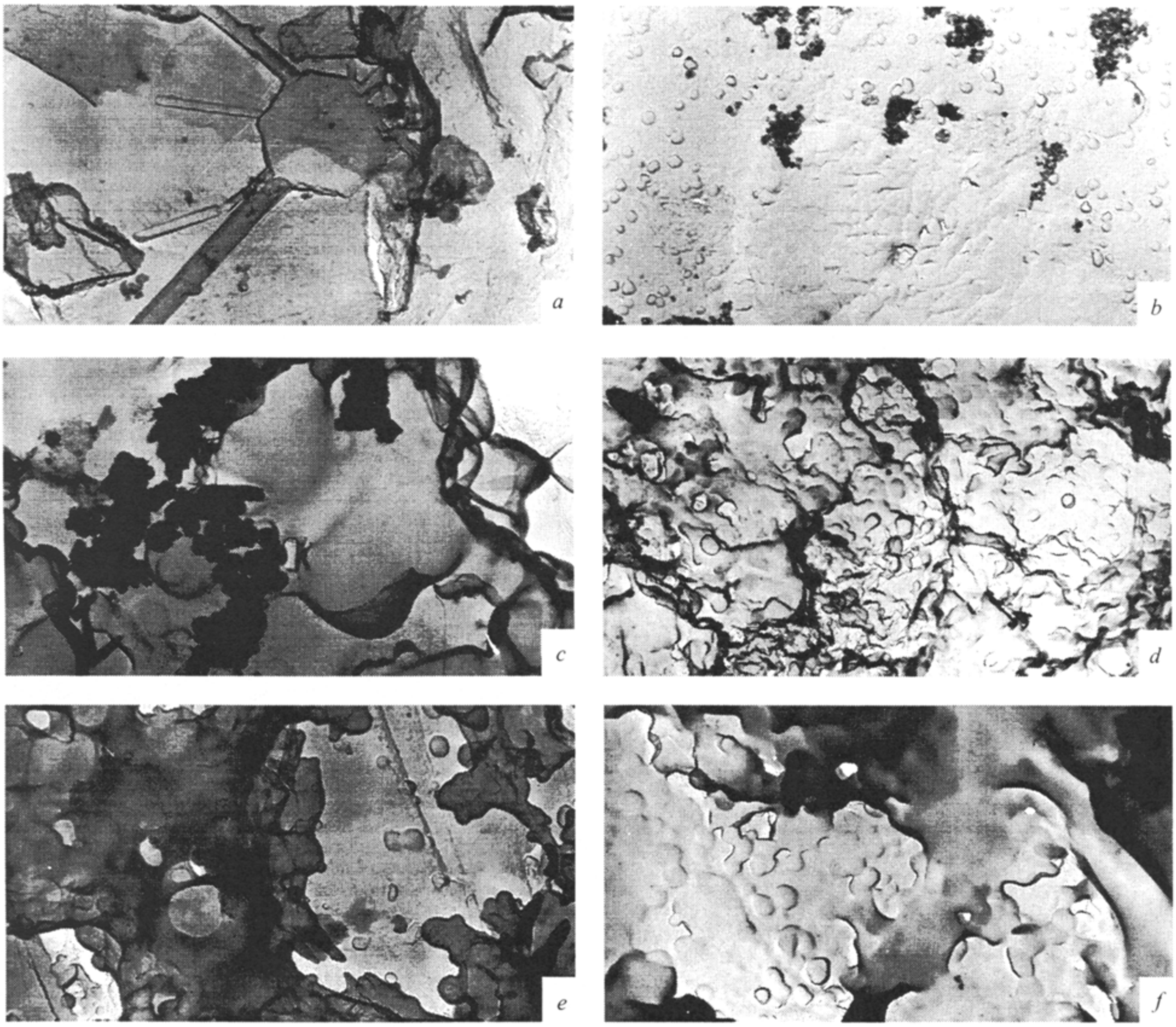

Fig. 2. Electron microscope photos of samples of mixtures 1 (*a*), 5 (*b*), 2 (*c*), 3 (*d*), 8 (*e*), and 11 (*f*) fired at a temperature of 1050°C. *a*, *b*) Magnification ×25,000; *c* – *f*) ×30,000.

of the sample (Fig. 2*b*) exhibit an increased content of the vitreous phase, which is clearly observed in comparing Fig. 2*a* and Fig. 2*b*.

The main structural elements of the fired Mitrofanovskii kaolin (Fig. 2*c*) are isometric grains of irregular shape 1 – 05 μm in size which are morphologically close to mullite crystals and crystal aggregates. Communicating pores 0.1 – 10.0 μm in size are located between the grains. This indicates that the formation of the material proceeds through a highly viscous vitreous phase.

The structure of the fired Zhana-Daurskii clay samples (Fig. 2*d*) has certain morphologic distinctions from the Mitrofanovskii kaolin samples (Table 3, mixtures 2 and 3): comparatively dense aggregates of sintered particles emerge here, which are divided by rare small slot-like pores. Apparently, sintering of the Zhana-Daurskii clay yields a greater amount of the vitreous phase than sintering of the Mitrofanovskii kaolin, which can be accounted by the peculiarities of the chemical composition of this clay, a lower content of the refractory material (Al_2O_3), and a higher content of Fe_2O_3.

The structure of the Mitrofanovskii kaolin samples with the optimum additive of bentonite (with the kaolinite : montmorillonite ratio equal to 1.16; Table 3, mixture 8) differs from the structure of the samples without the additive (Table 3, mixture 2). It contains areas of homogeneous sintered material with isolated, mostly sealed pores (Fig. 2*e*). The bentonite imparts a porous structure to the sample, in which isometric communicating pores (1.0 – 10.0 μm) prevail. The communicating channels are tortuous and numerous. Some of them originate from the slot-shaped pores which are typical of small samples, and others emerge in the course chilling due to the cracking of the ceramic mixture determined by its

stiffness and inhomogeneity (the presence of crystalline silica grains) [1].

The structure of the Zhana-Daurskii clay samples with the optimum bentonite additive (Table 3, mixture 11) and the kaolinite montmorillonite ratio equal to 1.45 differs from the structure of the samples without bentonite additive (Table 3, mixture 2) in having sites with the exocontact type of sintering (Fig. 2*f*). The sites of this type are located in the spaces between the "frame elements" [1]. Such structure, on the one hand, provides for high strength, and on the other hand, ensures relatively low water absorption, which is confirmed by the results of our studies (Fig. 1, curve *3*).

The formation of such a structure occurs under the conditions of the liquid phase formation. The cracking which is typical of bentonite is less probable in this case, since the sites with the exocontact type of sintering act as stress relaxers [1].

Thus, the additive of 30% bentonite to the non-sintering Mitrofanovskii clay decreases insignificantly the water absorption and does not lead to sintering at a temperature of 1150°C.

The optimum bentonite additive (30%) to the gravitation tails clay component that is capable of good sintering decreases insignificantly the water absorption. This is apparently due to the fact that the material contains a sufficient quantity of montmorillonite.

The introduction of montmorillonite to the Zhana-Daurskii clay has a perceptible effect, which is determined by the decrease in the temperature of the liquid phase formation and a decrease in viscosity. Moreover, the bentonite additive decreases the temperature of formation of new phases.

REFERENCES

1. I. V. Shalamova, V. F. Pavlov, and O. S. Grum-Grzhimailo, "A study of sintering of kaolinite clay – bentonite mixtures and development of low-temperature tile mixtures on this basis," *Publ. NIIstroikeramika Inst.*, 16 – 26 (1980).
2. V. Z. Abdrakhimov, *Production of Ceramic Articles Based on the Wastes from Power Engineering and Non-Ferrous Metallurgy* [in Russian], Ust'-Kamenogorsk (1997).
3. V. Z. Abdrakhimov, "Phase composition of facing tiles based on industrial waste," *Steklo Keram.*, No. 9, 21 – 22 (1990).
4. V. Z. Abdrakhimov, "Phase transformations in firing of ceramic tiles based on concentration waste," *Steklo Keram.*, No. 3, 23 – 24 (1992).